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**CELLULOSE FIBER-TO-FIBER AND FINES-IN-FIBER FLOCCULATION:  
A DYNAMIC COMPARISON**

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Dynamic Comparison

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ABSTRACT

The coagulation and flocculation tendencies of bleached kraft aspen fiber-to-fiber and fines-to-fiber systems have been studied simultaneously to determine their behavior as influenced by simple electrolytes, polyelectrolytes, pH, agitation, and fines addition levels. Although both of these systems can flocculate with cationic, anionic, or nonionic polyacrylamide polymer addition, it was demonstrated that with increased polymer concentration it is possible to maintain flocculation of the fines-to-fibers system, while simultaneously producing good fiber dispersion. The increased shear forces on the larger particles and their decreased relative surface area increases their redispersion response. The flocculation forces of the cationic polymer - cellulose system were strong enough to withstand the increased shear forces at high agitation, and because of the increased particle collision frequency and kinetic energy, less polymer was required to achieve maximum flocculation than at low agitation. The weakly interacting anionic and nonionic systems were not able to withstand the high agitation. The addition of coagulating electrolyte ( $\text{LaCl}_3$ ) reduced the amount of polymer required to give maximum fiber-to-fiber flocculation by compressing the electric double layers and reducing the effective surface area compared to that without electrolyte present. The fines-to-fiber systems were influenced in a similar manner with the added electrolyte; however, the cationic polymer produced less fines retention because of the adsorption competition with the cation of the electrolyte and the presence of weaker coagulation forces. In general, the pH influence on flocculation followed the charge state of the polymer functional groups with pH 5 being more effective for the cationic polymer and pH

9 for the anionic and nonionic polymers. Increasing the fines concentration to 10% greatly increased the degree of fiber flocculation as a result of extending polymer bridging effects.

## INTRODUCTION

There are two interacting systems of importance in the papermaking process: fiber-to-fiber and fines-to-fiber. These two systems greatly affect certain papermaking processes, such as sheet formation, water drainage, and fines retention (1-4). Poorly distributed fibers in the furnish will produce a sheet of localized basis weight variations, resulting in a sheet of poor optical and physical properties. Evenly distributed slurry fibers will result in a sheet of uniform fiber weight distribution. However, a highly dispersed fiber system results in large losses of fines during sheet formation just prior to mat formation (5-6). Thus, it is necessary to play off good sheet formation properties and good fines retention.

One of the main papermaking challenges thus is to find the best combination of proper sheet formation with adequate fines retention. Generally, it has been assumed that fines-to-fiber and fiber-to-fiber interactions are the same. Workers most often study fines-to-fiber systems and extrapolate results to fiber-to-fiber systems (2, 8-9).

The present study simultaneously measured interactions in the fines-to-fiber system and fiber-to-fiber system in order to establish similarities and/or differences. Fiber-to-fiber interactions were monitored via the variation of reflected light from a two branched fiber optics light probe, in a slightly modified manner (12) to that previously described (11). The fines-to-fiber

interactions were followed by monitoring  $C^{14}$  radioactively tagged fines remaining in the supernatant in a slightly modified manner (12) to that previously described (1).

Flocculation of particles is accomplished with polymers by the adsorption of segments of the polymer molecules on many different particles thus forming polymer bridges (10). These bridges must be able to withstand the applied shearing forces of the suspension to remain effective. Furthermore, it has been shown (1) that fines retention by fibers is a surface change controlled process when simple electrolytes are used as coagulants. Therefore, these systems were studied under the influence of polymer type and polymer concentration, electrolyte type and electrolyte concentration, fines addition level, agitation level, and pH.

Classified bleached kraft aspen fibers were used. The fines were from the same source as those prepared by Walkush and Williams (1) from  $C^{14}$  tagged bleached kraft aspen. Three test polymers were evaluated, one each of a cationic, anionic, and nonionic polyacrylamide. All polymers were of the same backbone structure and in the  $2-4$  million molecular weight range. The pH range evaluated was 5 to 9, with both a low and high agitation employed: the low agitation value lying on a broad plateau where fiber entanglement showed no dependence on agitation speed, while the high agitation was selected at a point of a large degree of fiber dispersion similar to results previously reported (11).

## RESULTS AND DISCUSSION

Suitable response to fiber-fiber interaction was found at consistencies ranging from 0.1 to 1.0% with 0.5% being selected for study. The response of the interaction to simple electrolyte concentration and cation valence was similar to that reported for cellulose fines retention by cellulose fibers (1), indicating

the significance of surface charge to fiber-fiber coagulation. The critical concentrations for coagulation found were  $2 \times 10^{-3}\text{M}$ ,  $3 \times 10^{-4}\text{M}$ , and  $1 \times 10^{-5}\text{M}$  for sodium, calcium, and lanthanum chlorides, respectively.

#### Polymer Without Added Electrolyte

The results for the fiber-to-fiber flocculation, with 1.0% fines based on fiber weight, by the three test polymers are presented in Fig. 1. Similar results were obtained also for these systems without the added fines. Results for the fines-to-fiber flocculation by the three test polymers at a 1.0% fines level are presented in Fig. 2.

[Fig. 1-2 here]

In comparing the systems, it is evident that the test polymers were effective flocculants in different ways. The fiber-to-fiber systems showed maximum degrees of flocculation at a certain polymer concentration with fiber redispersion upon increased polymer additions. However, although the polymers induced fines flocculation to the fibers, the fines remained attached to the fibers past the polymer concentrations where the fibers became redispersed. As proposed by Lamer and Smellie (10), the rate of disintegration of spherical particles is inversely proportional to the surface area of the particle. Increased surface area allows increased polymer adsorption, increasing polymer bridge strength, thus resulting in increased fines-to-fiber flocculation. Similarly, the smaller fines particles experience a smaller degree of disruption shear forces from slurry agitation than do the larger fiber particles, resulting in less floc disruption at the same agitation for the fines-to-fiber system than for the fiber-to-fiber system. This result is of significance, since it demonstrates that the desirable condition of good fiber dispersion while still maintaining good fines retention is possible. However, the possibility of achieving this in the mill needs further exploration.

Although redispersion of the fines particles was not achieved generally at the polymer concentrations studied, redispersion would be expected if the polymer concentrations were increased enough. The fines particles, with their large surface area, require greater polymer concentrations to achieve maximum flocculation, and thus more polymer to reach redispersion (13).

Based on surface area considerations, it had been anticipated that added fines would influence fiber-to-fiber flocculation. Since the 1.0% fines level did not produce changes, a study was made with 10.0% fines added to the system. This system was evaluated with cationic polymer at high agitation and pH 5. The degrees of fiber flocculation at 0, 10, and 20 parts per million (ppm) polymer were 0.45, 3.29, and 2.58, respectively, indicating a rather large fiber flocculation dependence on fines addition levels. It is of interest to note that the polymer concentration for maximum flocculation was the same as at 1.0% and zero fines systems, but the magnitude of flocculation was increased substantially. The limited amount of  $C^{14}$  tagged fines available prevented extension of the fines effect studies at this time.

It is felt that the above fines level results can be explained on the basis of an extended polymer bridge system, with the fines particles extending the bridging power of the polymer by forming networks of fiber-fines-polymer agglomerates. Since, the building units of the network with increased fines level would be larger and more extensive than with little or no fines, the entrapment and entanglement ability of the network would be increased. This fact, plus the fact that the longer bridging unit is a better flocculation unit than the shorter bridge (14), leads to increased flocculation with the increased fines.

The fines-to-fiber interactions were also evaluated at a 10.0% fines addition level with the cationic polymer at pH 5 and high agitation. Retention values of 11.7, 86.3, and 96.0% at 0, 10, and 20 ppm polymer, respectively, were observed indicating no difference from the 1.0% fines systems. Note that the fibers were dispersed while the fines were retained at 20 ppm polymer, as had been observed in the 1.0% fines systems.

Similarly, the 10% fines work supported the concepts of LaMer and Smellie (10) discussed above in that the size of the particle represents a factor tending to pull the network apart, while the surface area retards the decrease in network size by particle binding through increased polymer adsorption.

Polymer charge type was important in the flocculation of the cellulosic materials, with the cationic polyacrylamide being more effective than either the anionic or nonionic polymers, as seen in the way that agitation affected flocculation. Only the cationic polymer interacted with the cellulose strongly enough to maintain flocculation increases at the higher agitation. Micro-Kjeldahl measurements of the polymer retained by the fiber indicated that the adsorption of the positively charged cationic polymer by the negatively charged cellulose was more extensive than for the anionic or nonionic polymers. This floc strength effect is also seen in the result that fines retention was more complete at low agitation for the cationic system (96.0%) as compared with the anionic system (60.0%) and the nonionic system (55.0%), and in the result that at high agitation neither anionic or nonionic polymer effected fines flocculation.

Less cationic polymer was required to reach maximum fiber flocculation at high agitation compared with low agitation. Since the polymer-cellulose adsorption was strong enough to withstand the high agitation, the increased

particle collision frequency and kinetic energy at elevated agitation led to maximum flocculation at a lower polymer concentration.

There was a pH dependency for the fines-to-fiber interactions, but only for systems where retention had not yet reached the 90 to 100% range. The cationic polymer was a more effective flocculant at pH 5 compared with pH 9, while the anionic and nonionic polymers were more effective flocculants at pH 9 than at pH 5. Generally, the pH dependence followed the charge state of the polymer functional groups. The tertiary amine groups of the cationic polymer are more fully charged at pH 5 than at pH 9, and the carboxylic acid groups of the anionic and nonionic polymers are more completely ionized at pH 9 compared to pH 5. [The nonionic polymer is probably slightly anionic due to a small number of carboxylic acid groups produced during polymerization.] The cationic polymer interacted favorably with the negative cellulose surface. The anionic and nonionic polymers were effective at low agitation since there were apparently enough active adsorption centers on the cellulose surface and the like charge centers were far enough apart.

Dependency on pH by the fiber-to-fiber systems was not observed over the pH range of 5 to 9, probably because the experimental detection system was not sensitive enough to follow any small influence by pH change.

#### Polymer with Added Electrolyte

The results of the studies of the effect of polymer addition on the fiber-to-fiber and fines-to-fiber systems after coagulation to the maximum extent with  $\text{LaCl}_3$  electrolyte are presented in Fig. 3 and 4, respectively.

[Fig. 3-4 here]



For the fiber-to-fiber system, the influence of pH and agitation on flocculation by polymer in the presence of coagulating electrolyte was the same as observed where no electrolyte was present. Likewise, the flocculation responses to concentration of the polymers and the percentage changes in flocculation were the same. However, the cationic and anionic polymer concentrations required to achieve maximum flocculation were much lower (2 to 10 ppm) with  $\text{LaCl}_3$  present. The electrolyte has enabled system particles to approach more closely together by reducing the electric double layer influence, resulting in an increased likelihood of polymer bridges being formed. Also, by starting with coagulated fibers, the added polymer encounters larger particles, resulting in a reduced surface area. LaMer, et al. (13) have demonstrated that a lower flocculant concentration is required to achieve maximum flocculation as the surface area of the particle system is lowered.

Differences in flocculation responses in the fines-to-fiber systems with and without added electrolyte were not as straightforward. Notable differences for the cationic polymer included lower levels of retention with  $\text{LaCl}_3$ , and less retention at 585 rpm compared with 255 rpm. The anionic polymer showed a distinct fines retention at high agitation with  $\text{LaCl}_3$ , and a strong redispersion of the fines at 255 rpm, whereas neither effect was observed without the electrolyte. When  $\text{LaCl}_3$  was added to the nonionic systems, pH 9 became a better flocculation condition than pH 5, whereas is pH effects were seen without  $\text{LaCl}_3$ .

In the case of the cationic polymer these differences can be explained on the basis that the  $\text{La}(+3)$  cation was competing for the cationic adsorption sites on the cellulose; thus the cationic polymer probably became a less effective bridging agent because of lower adsorption. This competition would account for the reduced retention, since it is generally held that the networks formed by

electrolyte coagulation are not as resistant to disruptive shear forces from agitation as are the networks formed by polymer-cellulose interactions.

The anionic and nonionic polymers became better flocculants because the compression of the electric double layers allowed less interference of the like charges of the polymer and cellulose surface, possibly increasing adsorption of these polymers.

It has been demonstrated in this study that, with the proper combination of polymer type and polymer concentration, electrolyte conditions, agitation conditions, and pH, it may be possible to achieve significant levels of fines retention, while maintaining good fiber dispersion. Thus, it may be possible to gain significant improvements in sheet optical and physical properties while minimizing cellulosic material build-up in mill white water systems.

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#### LITERATURE CITED

1. Walkush, J. C., and Williams, D. G., Tappi 57(1):112(1974).
2. Han, S. T., and Chang, N. L., Tappi 52(4):688-93(1969).
3. Swanson, J. W., Consolidation paper web, Trans. Symp., Cambridge, England (2):741-72(1965).
4. Nerelius, L., Norman, B., and Wahren, D., Tappi 55(4):574(1972).
5. Rubin, M. M., Paper Trade J. 101(6):39(1935).
6. Strachan, J., Paper Maker 89: Ta 33(1935).

7. Strazdens, E., Tappi 55(12):1691(1972).
8. Britt, K. W., Tappi 56(3):83(1973).
9. Das, B. S., and Lomas, H., Pulp Paper Mag. Can. 74(8):95(1973).
10. LaMer, V. K., and Smellie, R. H., Jr., J. Colloid Sci. 13(6):589(1958).
11. Muhonen, J. M., and Williams, D. G., Tappi 56(10):117(1973).
12. King, C. A. Cellulose Fiber-to-Fiber and Fines-to-Fiber Interactions: Their Coagulation and Flocculation Tendencies as Affected by Electrolytes and Polymers in an Agitated Water Slurry, Doctor's Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1975.
13. LaMer, V. K., Smellie, R. H., Jr., and Lee, P.-K., J. Colloid Sci. 12(6):566(1957).
14. LaMer, V. K., and Smellie, R. H., Jr., Pure Appl. Chem. (Aust.) (13):112(1963).

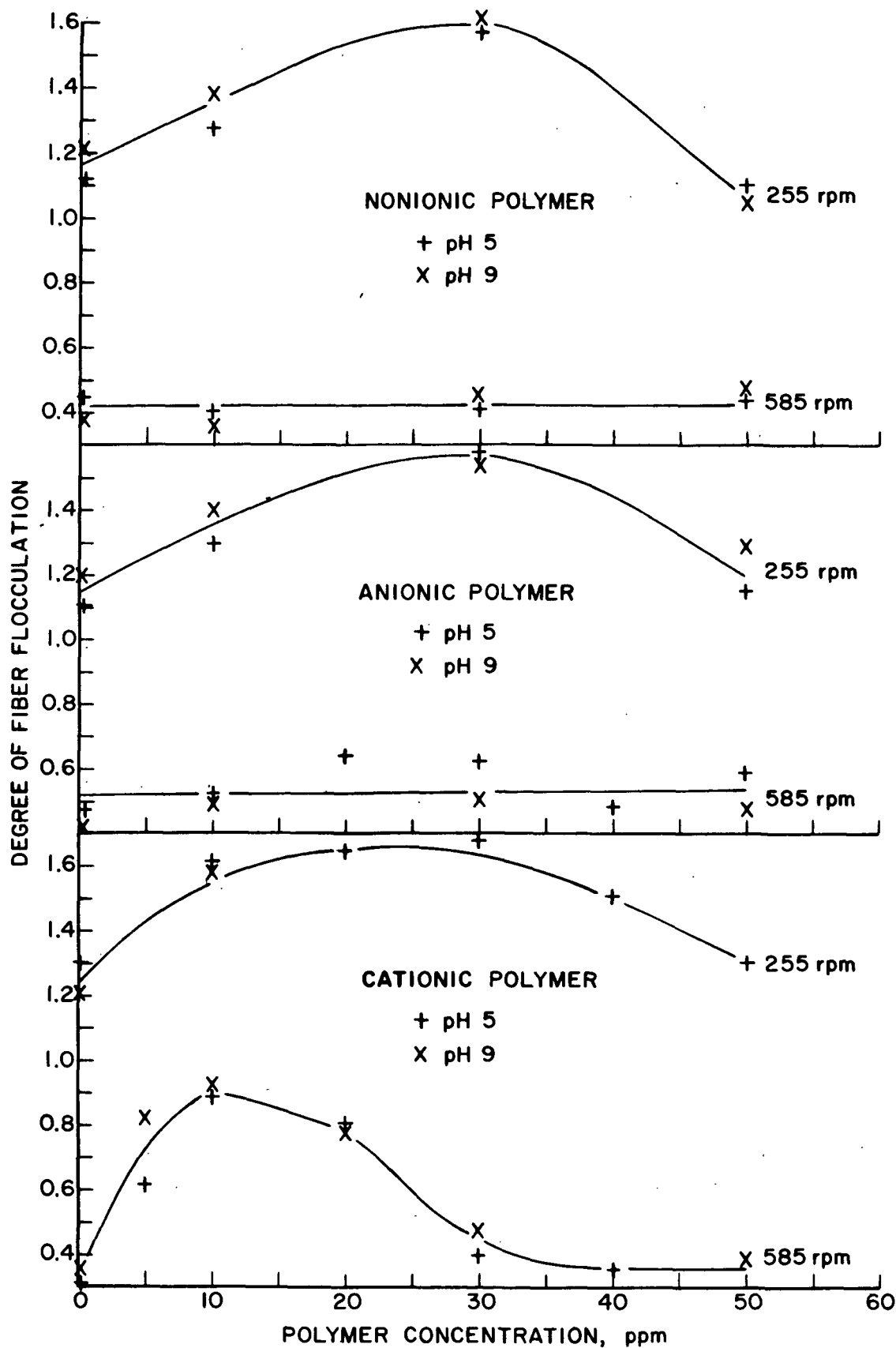


Fig. 1. Cellulose fiber-to-fiber interactions with 1% fines added as a function of polymer concentration, pH and agitation.

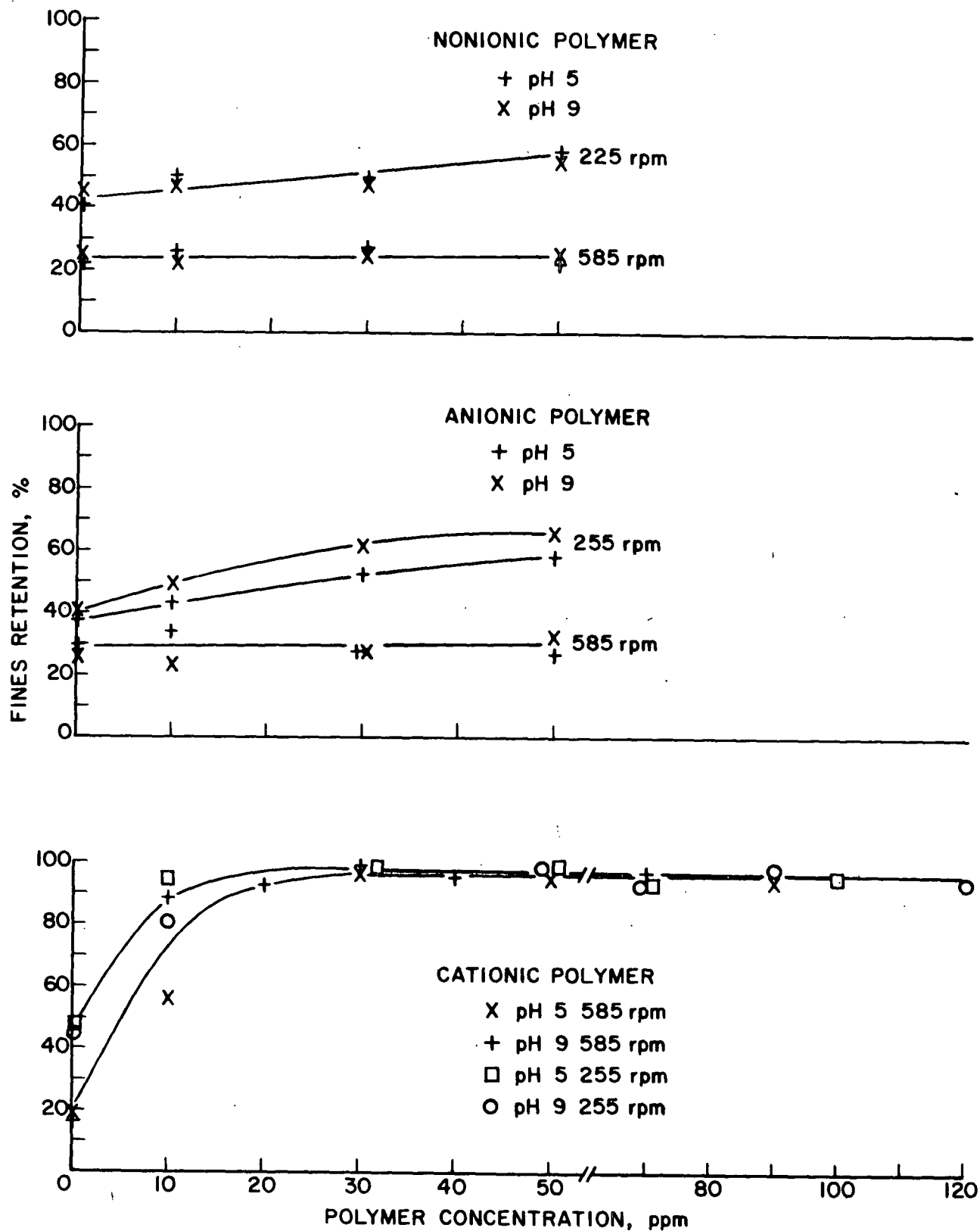


Fig. 2. Cellulose fines-to-fiber interactions with 1% fines added as a function of polymer concentration, pH and agitation.

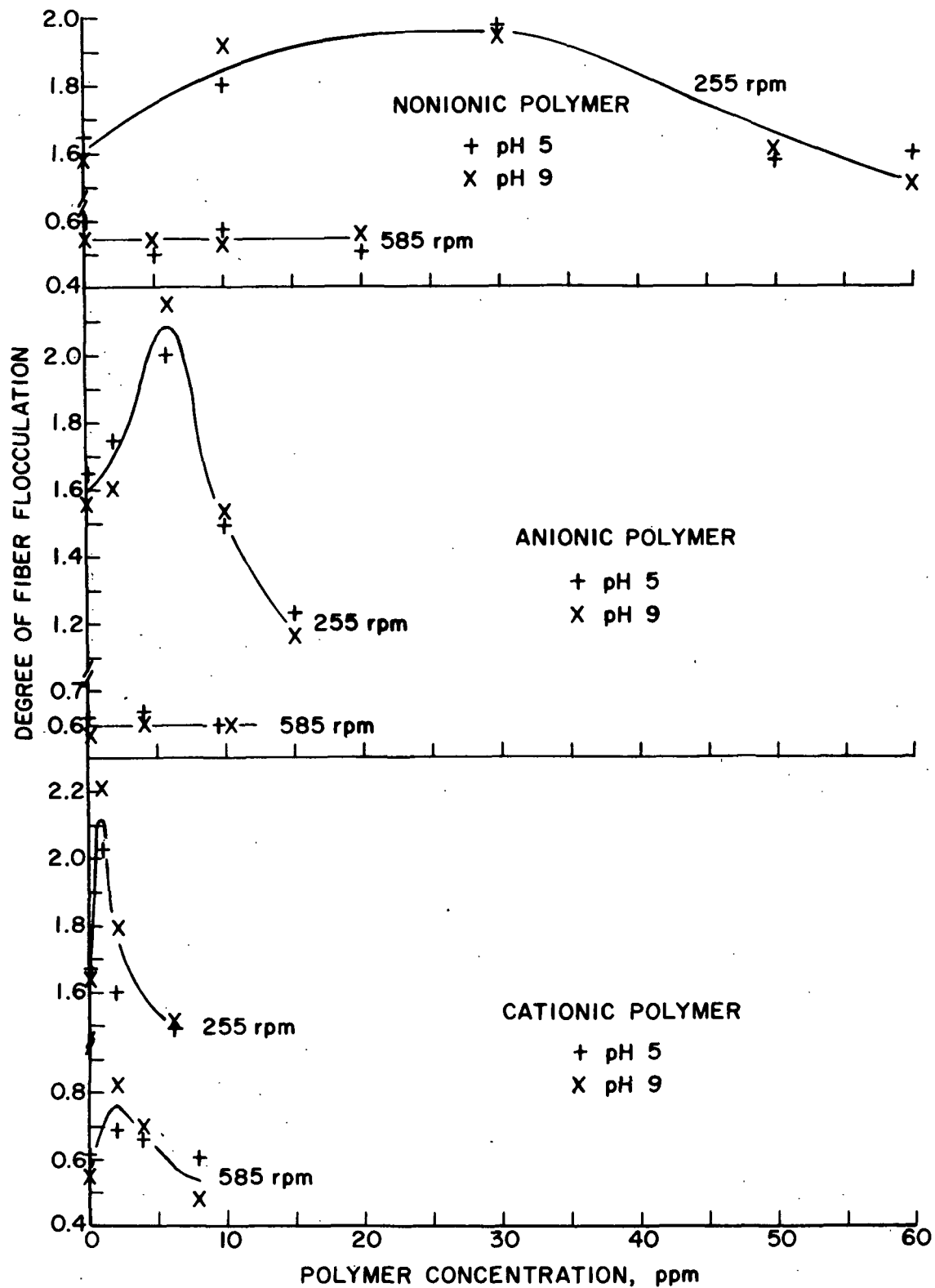


Fig. 3. Cellulose fiber-to-fiber interactions in  $1 \times 10^{-4}M$   $LaCl_3$  with 1% fines added as a function of polymer concentration, pH and agitation.

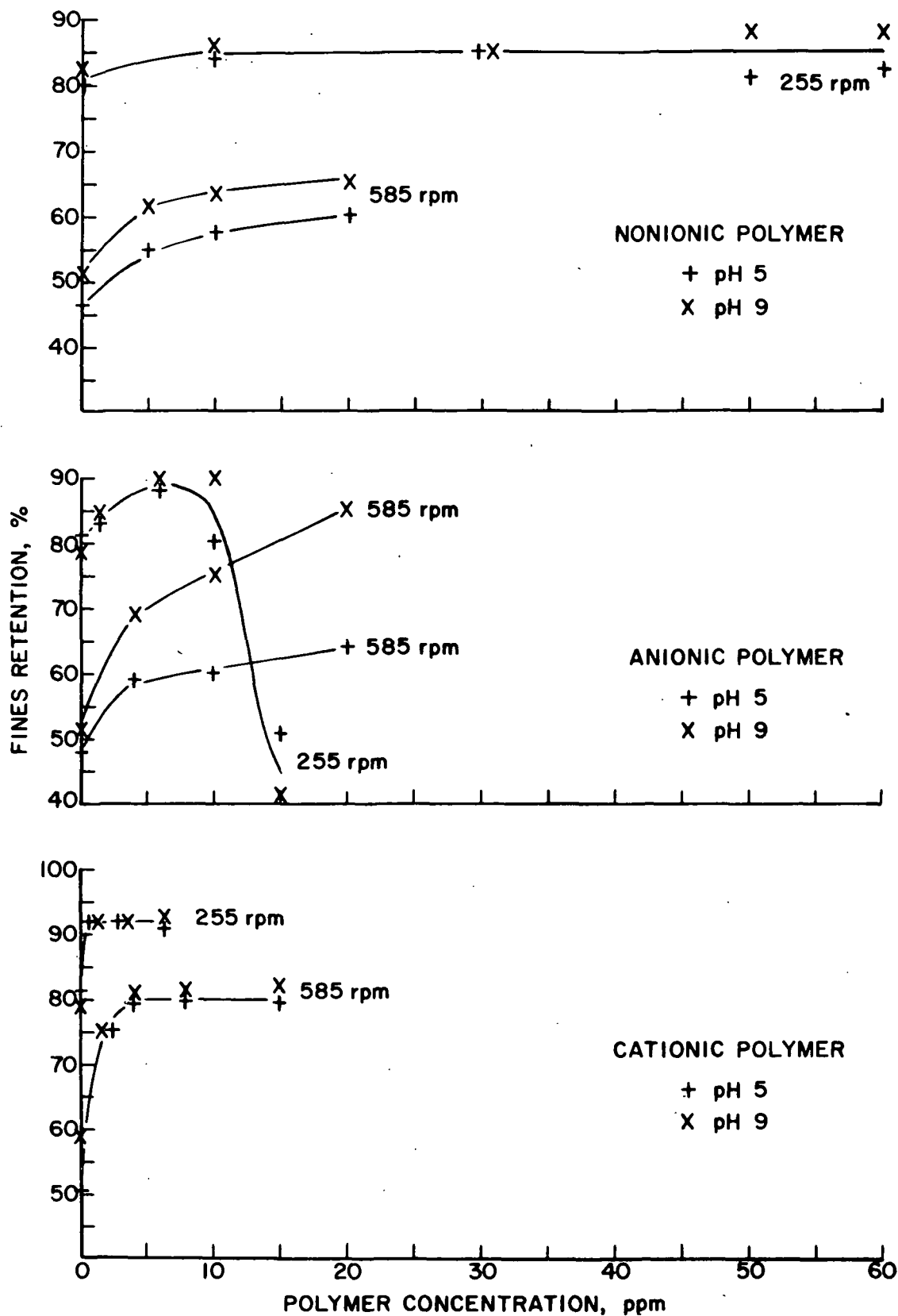


Fig. 4. Cellulose fines-to-fiber interactions in  $1 \times 10^{-4}$   $\text{LaCl}_3$  with 1% fines added as a function of polymer concentration, pH and agitation.